PB-217 444

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March 1971

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Environmental Protection Agency
Advanced Waste Treatment Research Laboratory
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ABSTRACT

Pilot treatment of District of Columbia primary effluent consisted of four-stage step aeration, alum addition in the final aeration pass for phosphorus removal, secondary clarification and multi-media filtration for tertiary solids separation.

The activated sludge system was operated with 4.0 hours aeration time (based on the influent flow) and an overflow rate in the secondary settler of 425 gal/(day)(sq. ft.). Alum ($Al_2(SO_4)_3 \cdot 14\ H_2O$) was dosed assuming an influent phosphous concentration of 8.15 mg/l as P. Lime (25 mg/l) was added to the mixed liquor to stabilize the wastewater during periods of low alkalinity. The dual-media filter (24-inch bed depth) and the tri-media filter (40-inch bed depth), each loaded at 2.4 gal/(min.)(sq. ft.), regularly exhibited filter runs between 24 and 32 hours.

When operating with the usual final stage mixed liquor pH (6.7 - 6.9), the complete system with tri-media filtration removed from the primary effluent 92% of the suspended solids, 96% of the BOD and 93% of the phosphorus. Daily fluctuations in the final stage pH, however, corresponded to similar fluctuations in phosphorus removal. Furthermore, the removal of suspended solids, BOD and phosphorus all increased to 97% during those periods when the final stage pH was between 6.3 and 6.6. Operation with a relatively low mixed liquor pH (less than 6.2), however, caused an upset in the activated sludge.

Key words:

Mineral (alum) Addition

Phosphorus Removal

Filtration

pH Control

Alum Addition To Activated Sludge With Tertiary Solids Removal*

By

Alan B. Hais, John B. Stamberg, and Dolloff F. Bishop**

The insolublization of phosphate ions in wastewater by the addition of aluminum salts to the activated sludge process is a low capital cost method for phosphorus removal. Barth and Ettinger (1) reported that sodium aluminate added to the aeration basin of an activated sludge pilot plant removed 95% of the phosphorus from a supplemented wastewater (0.5 mg./l. as P in the clarified effluent) at an aluminum to phosphorus weight ratio of 1.5:1. While an aluminum dose somewhat in excess of the stoichiometric weight ratio of 0.87:1 was necessary to obtain low phosphorus residuals, aluminum salt (mineral) addition to activated sludge had the advantage of a lower precipitant dosage than was required for an aluminum salt process incorporating a separate tertiary step for phosphorus removal. The improved settling characteristics of the combined biological and chemical sludge was also an advantage of mineral addition.

In a similar bench-scale pilot study, Eberhardt and Nesbitt (2) observed the effect of pH and filtration on phosphorus removal during mineral addition to the activated sludge process. In studies with domestic wastewater, operation with a mixed liquor pH of 6.0 and an aluminum to phosphorus weight ratio of 1.8:1 produced the greatest phosphorus removal after secondary clarification, averaging residuals of 0.5 mg./l. as P (96% removal).

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* Presented at the 68th National Meeting of the AIChE, Houston Texas March, 1971.

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Greater phosphorus residuals in the secondary effluent were recorded when operating with a mixed liquor pH between 6.1 and 6.8. However, laboratory filtration of the effluent samples increased phosphorus removals to greater than 99%, except when the pH was 6.8.

Miele (3) further confirmed the observation that phosphorus removal efficiency depended on pH. Short-term operation of a 1.8 million gal./day activated sludge plant with an average aluminum to phosphorus weight ratio between 1.4:1 and 1.8:1 produced phosphorus removals in excess of 95%. Jar tests indicated that greater phosphorus removal occurred with decreasing pH in the pH range of 5 - 8.

In the present study, alum (aluminum sulfate) was dosed at a constant rate to a 2,000 gal./day activated sludge pilot plant. In addition to conventional secondary settling, filtration was used to remove residual organic solids and particulate phosphorus. The effect of pH on phosphorus removal was established.

Pilot Plant

The pilot process (Figure 1) consisted of step aeration, secondary settling and filtration. Primary effluent from the main District of Columbia sewage treatment plant was fed at a constant rate to a four pass step-aeration system. A splitter box distributed equal portions of the primary effluent to each of the final three aeration passes. The fourth pass mixed liquor flowed by gravity to a circular settler, where it entered through a single port on the periphery of the clarifier and was baffled downward. The secondary settled solids were returned to the head of the first pass for reaeration. Because of the relatively small capacity of the clarifier, solids were wasted from the

first pass.

The overflow from the secondary clarifier was pumped to two pressurized plexiglas filter columns (6.5-inch i.d.) which were operated in parallel. One filter had a dual-media bed, packed with 18 inches of 0.9 mm. coal on top of 6 inches of sand (equal quantities 0.40-0.45 mm. sand and 0.8-1.20 mm. sand). The other filter was a "Neptune Microfloc" multi-media filter consisting of 2' inches of coal followed by ten inches of sand and five inches garnet (manufacturer's designation MF197). The flow rates, detention times, and hydraulic loadings for the processes are described in Table 1.

Alum ($Al_2(SO_4)_3 \cdot 14H_2O$) in an aqueous solution was added to the fourth pass mixed liquor to precipitate phosphate ions from the sewage. With the exception of one short period, alum was dosed at a constant rate for the entire operation. The alum dose was based on a 2:1 Al:P weight ratio and an influent phosphorus concentration of 8.2 mg./l. as P. An emergency lime feed system was installed after the third month of operation to increase the buffer capacity of the wastewater during periods of low alkalinity by adding 25 mg./l. of lime to the first pass mixed liquor.

Analytical Procedures

All samples for analysis were manually composited over 24 hours. During compositing, all samples were stored at $3^{o}C$ to minimize additional biological activity.

In the laboratory, the total phosphorus was determined by the persulfate method (4), BOD's by the probe method (5), ammonia (5) and nitrate-nitrite (6) were determined on the Technicon Automatic Analyzer, and the total organic carbon (TOC) was measured on a Beckman Carbonaceous Analyzer (7). All other analyses employed Standard Methods (8).

Operation of the Activated Sludge Process

The alum activated sludge process was started in August 1970, using primary effluent from the District of Columbia plant and seed biological solids from an existing step aeration process. Two weeks later, alum addition was begun; scheduled wasting of secondary settled solids began in the last week of August.

The operation of the activated sludge for the five-month period following the month of startup is summarized in Table 2. During the study, the Solids Retention Time (SRT) in aeration was operated at or above 5 days because operation of activated sludge on the District of Columbia wastewater produced filamentous growth and bulking solids for operation with SRT's between two and five days. The average MLSS for the first four months of operation was 6,600 mg./l. In January, increased solids wasting reduced the MLSS to less than 5,000 mg./l. and the SRT to 5.0 days. The percent volatile solids in the mixed liquor stabilized at approximately 60%. With an average sludge volume index of 45 for the entire operation, the solids were settleable.

Because of the relatively small scale of the system, meaningful clarification rates were not produced in the secondary clarifier. Settling rates were determined in one liter graduate cylinders. In a typical settling test, at a mixed liquor temperature of 9°C (lowest operating temperature), the initial portion of the subsidence was characterized by unhindered settling (Figure 2). After approximately 3.5 minutes, zone settling developed with a rate (based on the initial portion of hindered settling) of 13.2 ft./hr. (2,380 gal./(day)(sq. ft.)).

The presence of almost 8 mg./l. of NO_3^--N in the secondary effluent during September (Table 3) indicated that substantial nitrification was possible in a mineralized activated sludge with a final stage pH of less than 7. Gradually decreasing nitrate concentrations with corresponding increases

in NH_3-N were recorded as the temperature dropped during October and November. An upset in the activated sludge system in November destroyed many of the nitrifying organisms and nitrification was greatly reduced. The cold temperatures experienced during December and January prevented the recovery of the nitrifiers and nitrification never returned to the levels seen prior to the upset.

Pollutant Residuals

The activated sludge system with mineral addition performed well during the entire operation (Table 4). The slightly reduced performance of the system in November was caused by an upset in the activated sludge.

Good secondary treatment with filtration on stream was obtained during October, December and January. During these three months, secondary treatment alone removed 89% of the primary effluent BOD with filtration increasing the total removal to 96%. These treatment efficiencies produced average BOD values of 11.9 mg./l.in the secondary effluent and 5.0 mg./l. in the filtered (tri-media) effluent. An average TOC residual of 17.1 mg./l. in the secondary effluent represented 82% removal from the primary effluent. Filtration (tri-media) increased the TOC removal by 5% producing water containing an average of 11.8 mg./l. of TOC. Similarly, secondary treatment and filtration (tri-media) removed 82 and 90% of the influent COD, respectively, with COD residuals of 48.9 mg./l. in the secondary effluent and 27.4 mg./l. in the filtered effluent.

Secondary treatment removed 68% of the suspended solids from the primary effluent for an average residual of 33 mg./l. Filtration (tri-media) removed an additional 24% of the suspended solids with an average residual of 8 mg./l. Total phosphorus residuals averaged 1.9 mg./l. as P (78% removal) in the secondary effluent and 0.61 mg./l. (93% removal) after filtration (tri-media).

Operations during December provide an indication of typical variability in pollutant removal. BOD residuals ranged from 6.8 to 19.2 mg./l. in the secondary effluent with an average of 12.0 mg./l. for the month (Figure 3). Similarly, daily BOD residuals in the filtered (tri-media) effluent varied from 10.5 to less than 1 mg./l. for a monthly average of 4.9 mg./l. The suspended solids in the secondary effluent (Figure 4) exhibited greater daily variability than residual BOD ranging between 12 and 54 mg./l. (33 mg./l. average). Filtration (tri-media) reduced the solids to an average of 8 mg./l., although the quality of the filtered (tri-media) effluent (daily residuals from 1 to 29 mg./l.) reflected the variation in amount of suspended solids carried over from the secondary clarifier. The phosphorus removal exhibited an even greater daily variability than did the solids removal, with residuals ranging between 0.9 and 4.6 mg./l. as P in the secondary effluent and between 0.07 and 2.9 mg./l. as P after tri-media filtration (Figure 5). Nevertheless, phosphorus residuals averaged 1.9 mg./l. as P in the secondary effluent and 0.65 mg./l. as P in the filtered effluent.

Filter Media Comparison

Comparing the different filters, tri-media filtration removed between 5 and 10% more of the pollutant residuals from the secondary effluent than did dual-media filtration (Table 5). For the four months of filter operation, the tri-media effluent averaged 10 mg./l. of suspended solids and 0.7 mg./l. as P of total phosphorus, the dual-media effluent 13 mg./l. of suspended solids, and 0.89 mg./l. as P of total phosphorus. The phosphorus concentration in the tri-media filter effluent regularly duplicated the "soluble" phosphorus residual as determined by 0.45 u millipore filtration.

Similar differences in effluent quality from the two types of filters were observed with respect to the organic residuals (BOD, TOC, and COD). The residuals of BOD, TOC, and COD in the tri-media filter effluent averaged 5.8, 12.2, and 28.7 mg./l., respectively; the same residuals after dual-media filtration averaged 6.9, 12.2, and 34.4 mg./l.

With good quality secondary effluent (25 - 40 mg./l. suspended solids), filter runs between 24 and 32 hours occurred regularly. Filter runs in excess of 48 hours were possible during those periods when good phosphate precipitation and effective secondary solids capture in the settlers produced a very high quality secondary effluent (15 - 20 mg./l. suspended solids). During high solids carryover from the settlers (≥ 50 mg./l.), filter runs of 24 hours permitting solids breakthough still selectively removed phosphorus.

The Effect of pH

The fourth pass-mixed liquor pH for the five months of operation normally varied between 6.7 and 6.9. However, lower residuals of suspended solids and organics, as well as phosphorus, were recorded in the secondary and filtered effluents when operating with a fourth pass mixed liquor pH of less than 6.6. As an example of favorable pH operation, the twenty-day period from October 21 to November 9, at a pH of approximately 6.5 in the fourth pass mixed liquor, averaged filtered residuals of 4 mg./l. for suspended solids, 3.6 mg./l. for BOD, and 0.23 mg./l. as P for total phosphorus.

As the fourth pass pH increased to 7 and above, a deterioration of effluent quality was observed visually as well as by increased pollutant residuals. Operation at a relatively high pH (greater than 6.9) generally produced a fine turbid haze in the secondary effluent which was difficult to remove by filtration. During periods of high pH operation, the greatest increases were recorded in the residuals of suspended solids and phosphorus

while the residual organic concentrations were less affected.

Using the January fourth pass pH and filtered phosphorus residual as reference, a steady increase in the phosphorus residual corresponded to a similar rise in pH (Figure 6). Furthermore, many local peaks in the residual phosphorus concentration reflected similar peaks in the pH. Inasmuch as alum was fed at a constant rate, the only changes in the Al:P ratio were caused by normal fluctuations in the influent phosphorus concentration and the Al:P ratio randomly oscillated about the 2:1 value chosen for the study, averaging 1.99:1 for the month.

A definite relationship between the fourth pass pH and the filtered phosphorus residual is indicated by the smooth curve drawn through the data (Figure 7). The figure clearly defines the steady rise in phosphorus residual with pH. Furthermore, this increase in phosphorus residual is particularly rapid above pH 6.6.

Operation at pH below 6.2, however, produced an upset in the biological system. This upset occurred in November when the decreased buffer capacity of a rain-diluted sewage caused an excessive drop in pH at the 2:1 Al:P ratio being used for the study. Fourth pass pH values of 6.1 or less were recorded on several occasions during the second week of November. The pH values of the other mixed liquor passes, which normally exhibited the pH of the influent wastewater, were also reduced to the same level as the fourth pass pH.

On November 12, the Al:P ratio was reduced to stabilize the pH above 6.5 until the buffer capacity of the sewage returned to normal levels. However, the activated sludge mixed liquor had already been upset. When viewed under a microscope, the mixed liquor during this period appeared to be poorly bio-flocculated and the MLSS dropped from 7200 mg./l. to a low of 3850 mg./l. on November 22. The emergency lime feed system was installed shortly thereafter

and prevented a similar occurrence during a period of heavy rainfall in December.

The information derived from this study indicates that pH control is essential to consistently produce low phosphorus residuals from the alum addition activated sludge process. The control of pH in the relatively narrow range between 6.3 and 6.6 would necessitate alternate dosing of acid and base as required by the prevailing conditions of pH and alkalinity. Furthermore, with proper pH control, it is likely that efficient phosphorus removal can be achieved using an Al:P ratio considerably less than 2:1.

Summary

Step aeration with alum addition followed by secondary sedimentation and tri-media filtration with the fourth pass mixed liquor pH typically between 6.7 and 6.9 produced filtered effluent residuals of 5 mg./l. of BOD, 12 mg./l. of TOC, 27 mg./l. of COD, 8 mg./l. of suspended solids, and 0.6 mg./l. of total phosphorus(as P) for three months of stable operation. These residuals correspond to removals of 96, 87, 90, 92 and 93%, respectively, of the pollutants in the influent primary wastewater.

When operating with a fourth pass pH between 6.3 and 6.6 the pilot system (with tri-media filtration) removed 97% of the suspended solids, BOD, and total phosphorus from the District of Columbia primary effluent. The pollutant residuals after filtration for the twenty days of continuous operation in this pH range were 4 mg./l. of suspended solids, 3.6 mg./l. of BOD and 0.23 mg./l. as P of total phosphorus.

Dual- and tri-media filtration both provided effective tertiary solids separation, however, the tri-media filter consistently removed between 5 and 10% more of the pollutant residuals from the secondary effluent than did the dual-media filter. Filter runs between 24 and 32 hours were

maintained on a regular basis. Furthermore, with high quality secondary effluent, filter runs exceeding 48 hours were possible.

Fluctuations in the residuals of suspended solids and phosphorus corresponded to similar fluctuations in the fourth pass mixed liquor pH. A definite relationship between pH and phosphorus removal was then established, indicating that above pH 6.6 a rapid increase in the phosphorus residual occurred with increasing pH. However, operation with a mixed liquor pH of less than 6.2 caused an upset in the activated sludge. Therefore, it appears that optimum performance of the mineral addition activated sludge process is achieved by maintaining an average final stage pH between 6.3 and 6.6.

Nomenclature

BOD = 5-day biological oxygen demand

COD = Chemical oxygen demand

MLSS = Mixed liquor suspended solids

MLVSS = Mixed liquor volatile suspended solids

SS = Suspended solids

SRT = Solids retention time

SVI = Sludge volume index

TKN = Total Kjeldahl nitrogen

TOC = Total organic carbon

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Table 1. Operating Conditions

Process	Flow	Loading Rate
Secondary Settling	1.45 gal./min.	425 gal./(day)(sq.ft)
Filtration	0.56 gal./min.	2.4 gal./(day)(sq.ft)

Aeration time-4.0 hours (based on 1.45 gal./min. flow).

Return solids rate-42%

Table 2. Activated Sludge Operation

	Temp. ^{o}F	MLSS (% volatile) mg./l.	SVI	SRT days	F/M $\frac{\text{(lb.BOD used/day)}}{\text{lb. MLVSS}}$
September, 1970	81^{o}	6900 (59%)	65	6.5	0.15
October, 1970	75^{o}	6560 (59%)	36	8.7	0.16
November, 1970	68^{o}	5720 (60%)	37	6.4	0.19
December, 1970	63^{o}	7080 (59%)	44	7.4	0.18
January, 1971	54^{o}	4930 (60%)	44	5.0	0.24

Table 3. Nitrification

	Temp. °F	SRT days	Total Nitrogen Primary Influent mg./l.	Residuals TKN mg./l.	Residuals NH_3-N mg./l.	Residuals NO_3-N mg./l.
September, 1970	81°	6.5	25.8	8.5	6.9	7.9
October, 1970	75°	8.7	27.8	12.6	10.2	7.4
November, 1970	68°	6.4	26.2	13.2	11.0	6.5
December, 1970	63°	7.4	27.1	16.8	15.1	3.8
January, 1971	54°	5.0	26.5	16.6	14.3	3.4

Table 4. Residuals in effluents

	BOD mg./l.	TOC mg./l.	COD mg./l.	SS mg./l.	P mg./l.
September					
Primary	107	99	260	105	8.2
Secondary	12.2	11.3	33.9	19	1.4
October					
Primary	121	101	304	120	9.1
Secondary	16.2	17.5	54.3	41	2.2
Filtered (tri-media)	5.2	12.1	28.1	9	0.58
November					
Primary	128	92	280	97	8.7
Secondary	17.8	20.8	58.7	50	2.9
Filtered (tri-media)	8.1	13.6	32.6	16	0.97
December					
Primary	140	91	260	94	8.5
Secondary	12.0	16.4	47.0	33	1.9
Filtered (tri-media)	4.9	11.4	26.0	8	0.65
January					
Primary	127	85	255	96	8.2
Secondary	13.5	17.7	45.5	26	1.6
Filtered (tri-media)	5.0	11.9	28.1	7	0.61

Table 5. Filtration residuals

	BOD mg./l.	TOC mg./l.	COD mg./l.	SS mg./l.	P mg./l.
October					
Dual-media	5.2	11.7	35.5	14	0.68
Tri-media	5.2	12.1	28.1	9	0.58
November					
Dual-media	10.4	15.6	36.8	19	1.2
Tri-media	8.1	13.6	32.6	16	0.97
December					
Dual-media	6.3	12.6	28.6	11	0.97
Tri-media	4.9	11.4	26.0	8	0.65
January					
Dual-media	5.8	12.8	32.6	8	0.75
Tri-media	5.0	11.9	28.1	7	0.61

Figure 1. Pilot process for phosphorus removal.

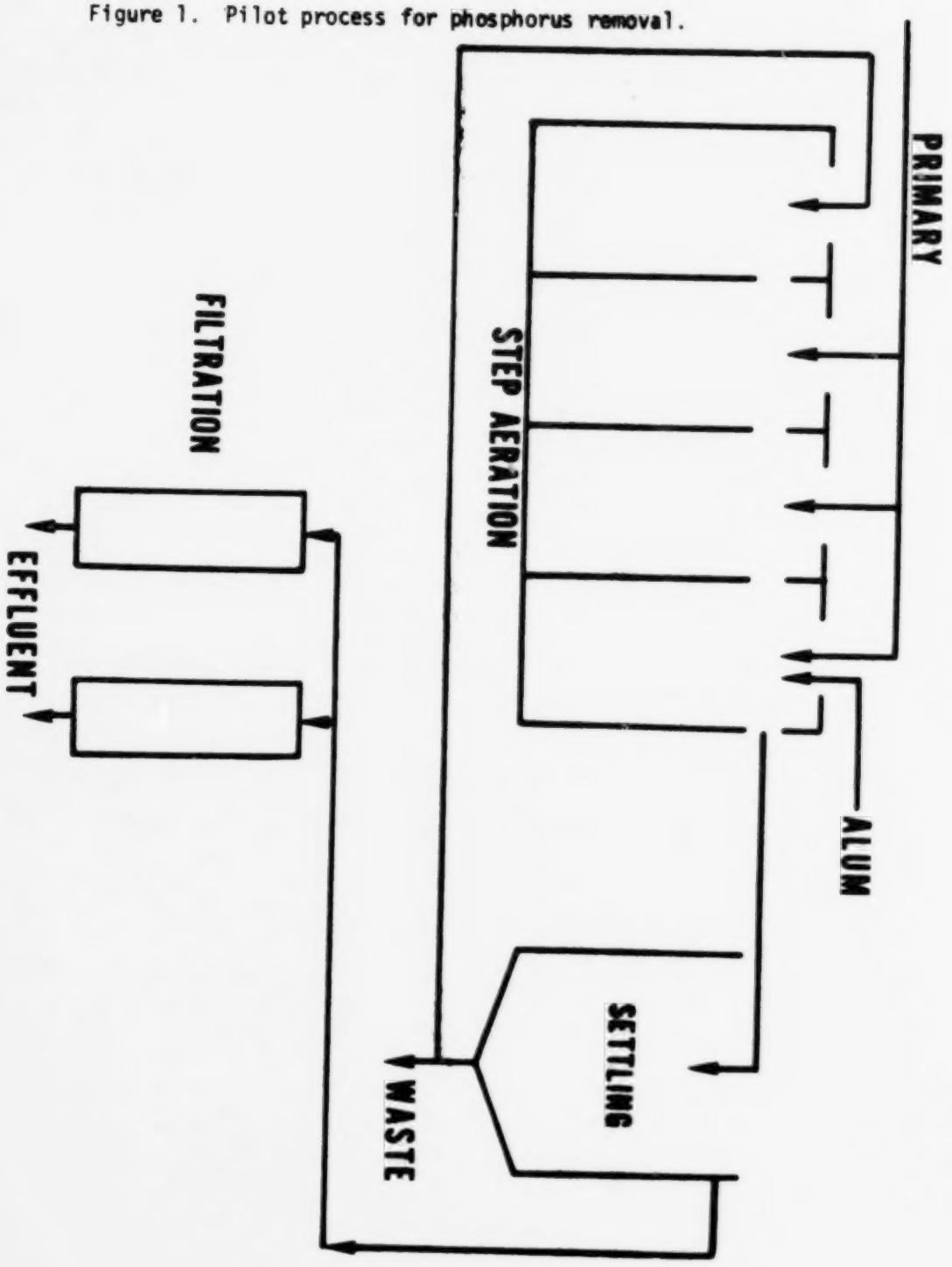

Figure 2. Settling test interface versus settling time.

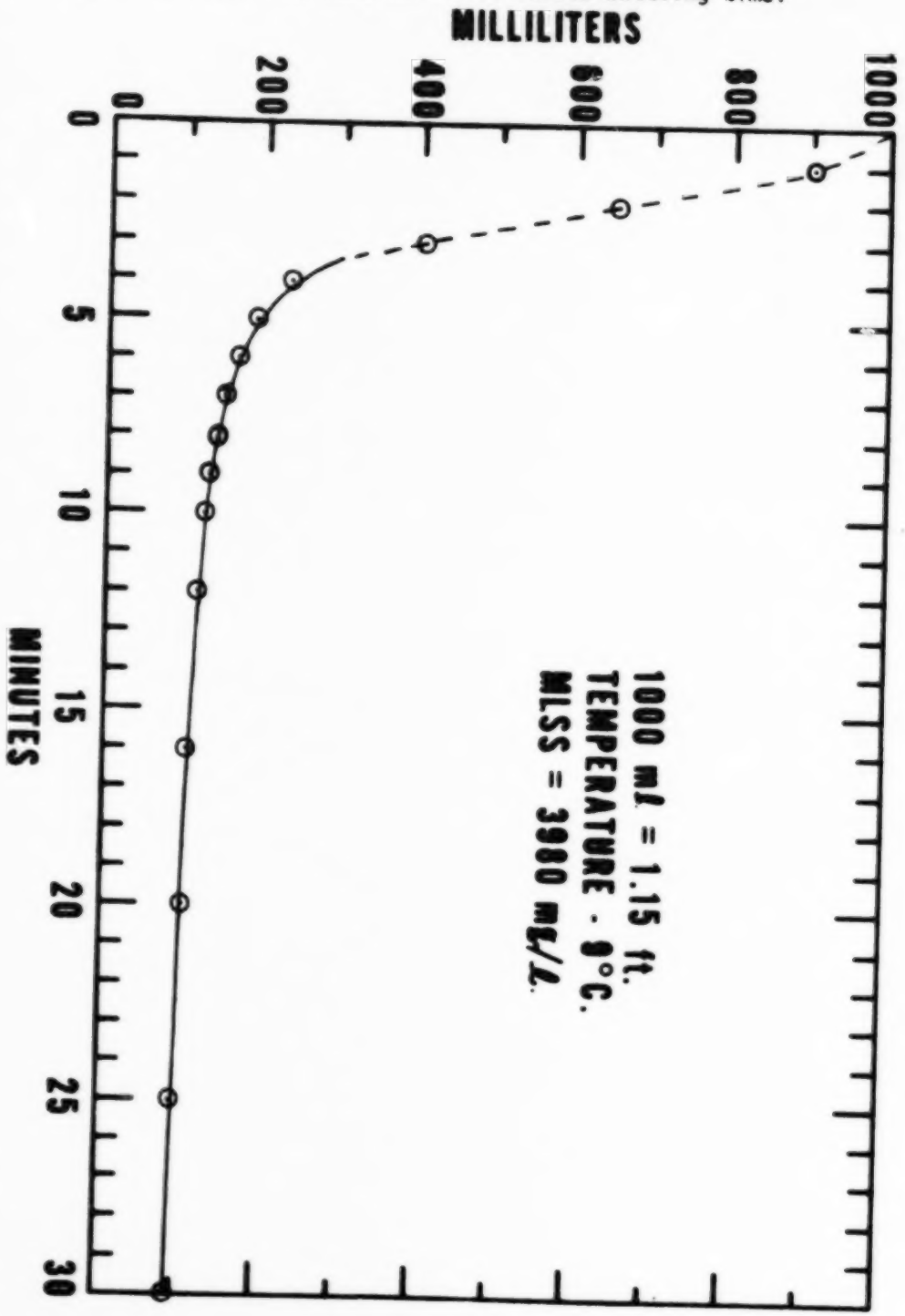

Figure 3. BOD removal during December.

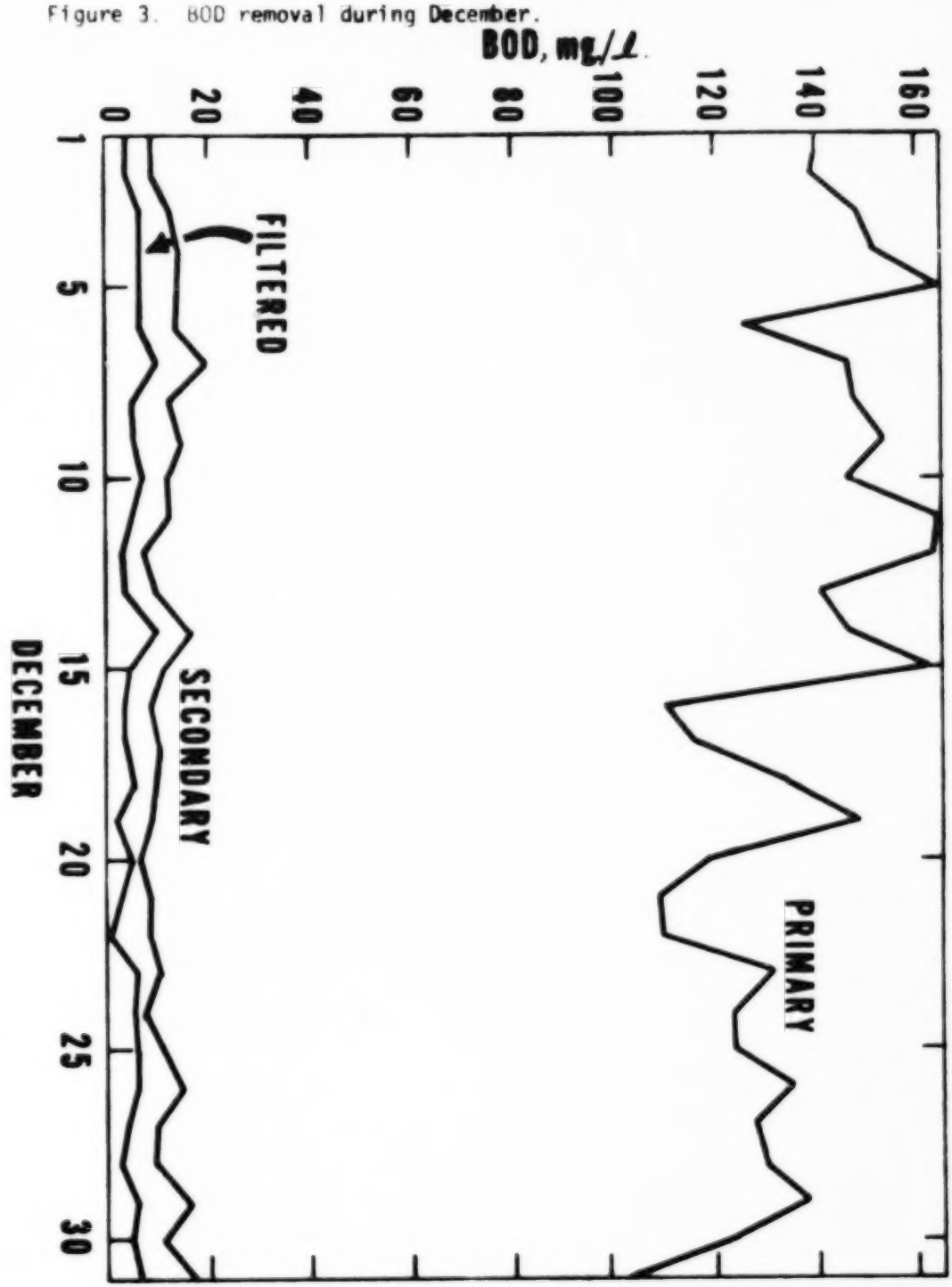

Figure 4. Suspended solids removal during December.

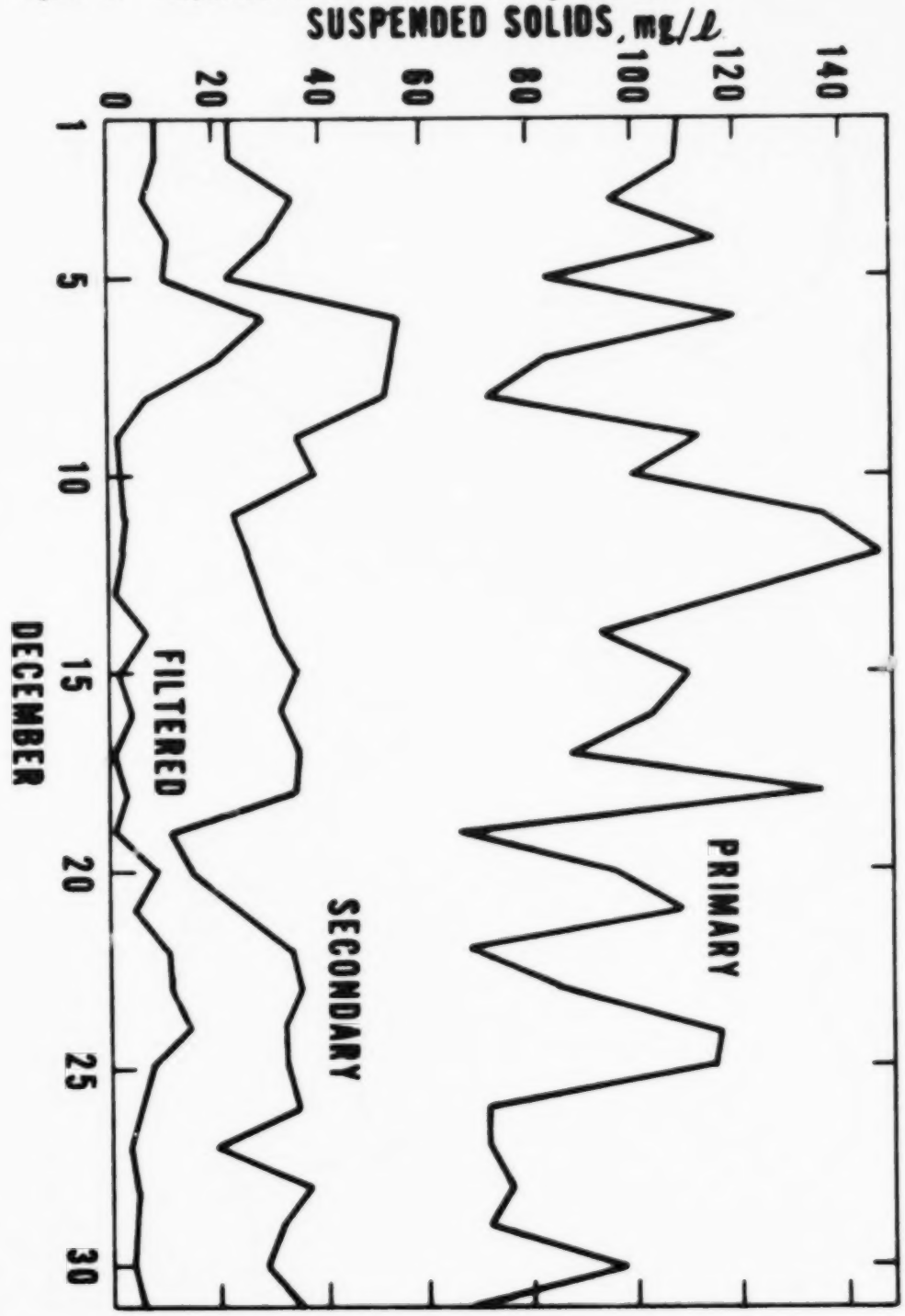

Figure 5. Phosphorus removal during December.

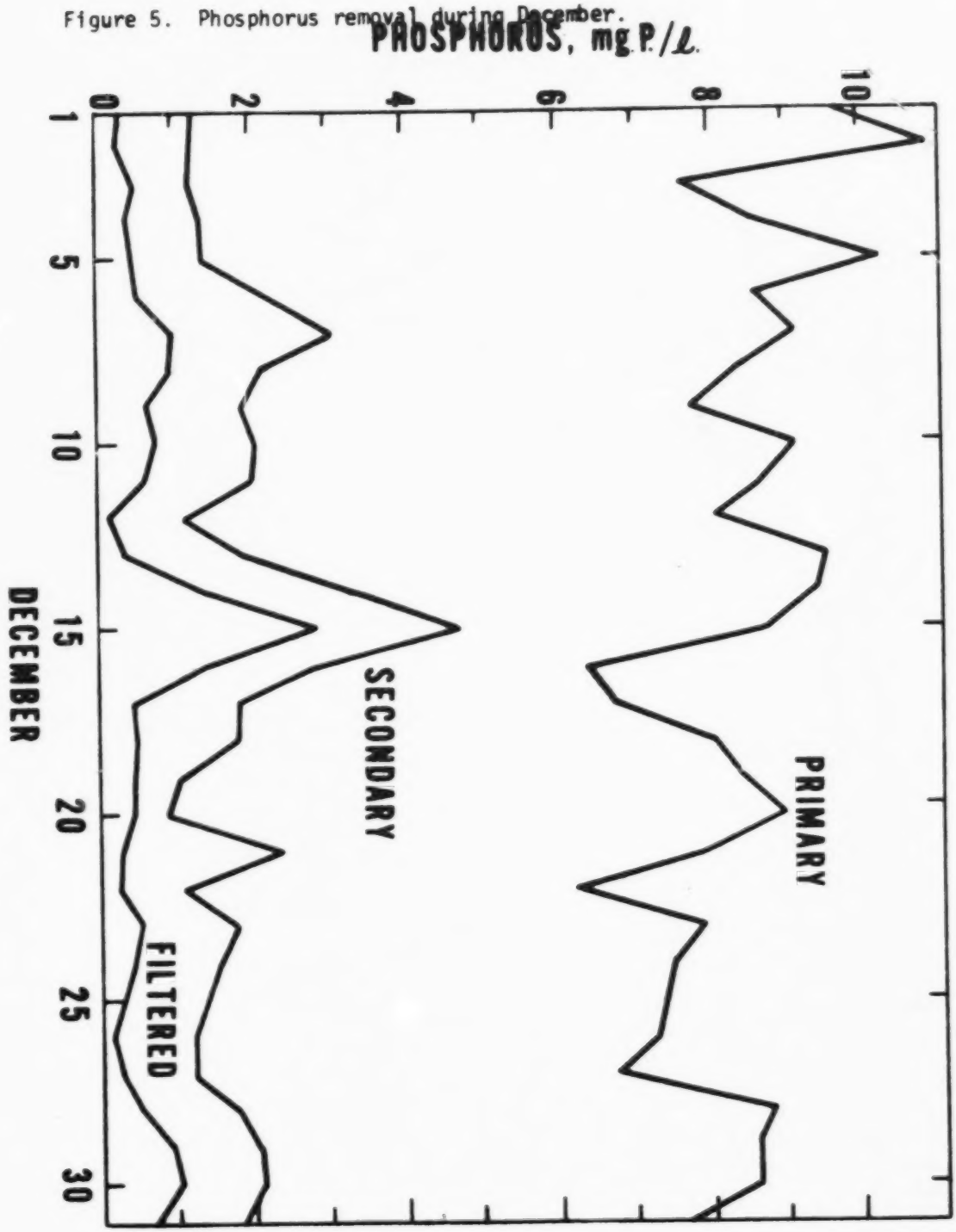

Figure 6. Phosphorus and pH variation during January.

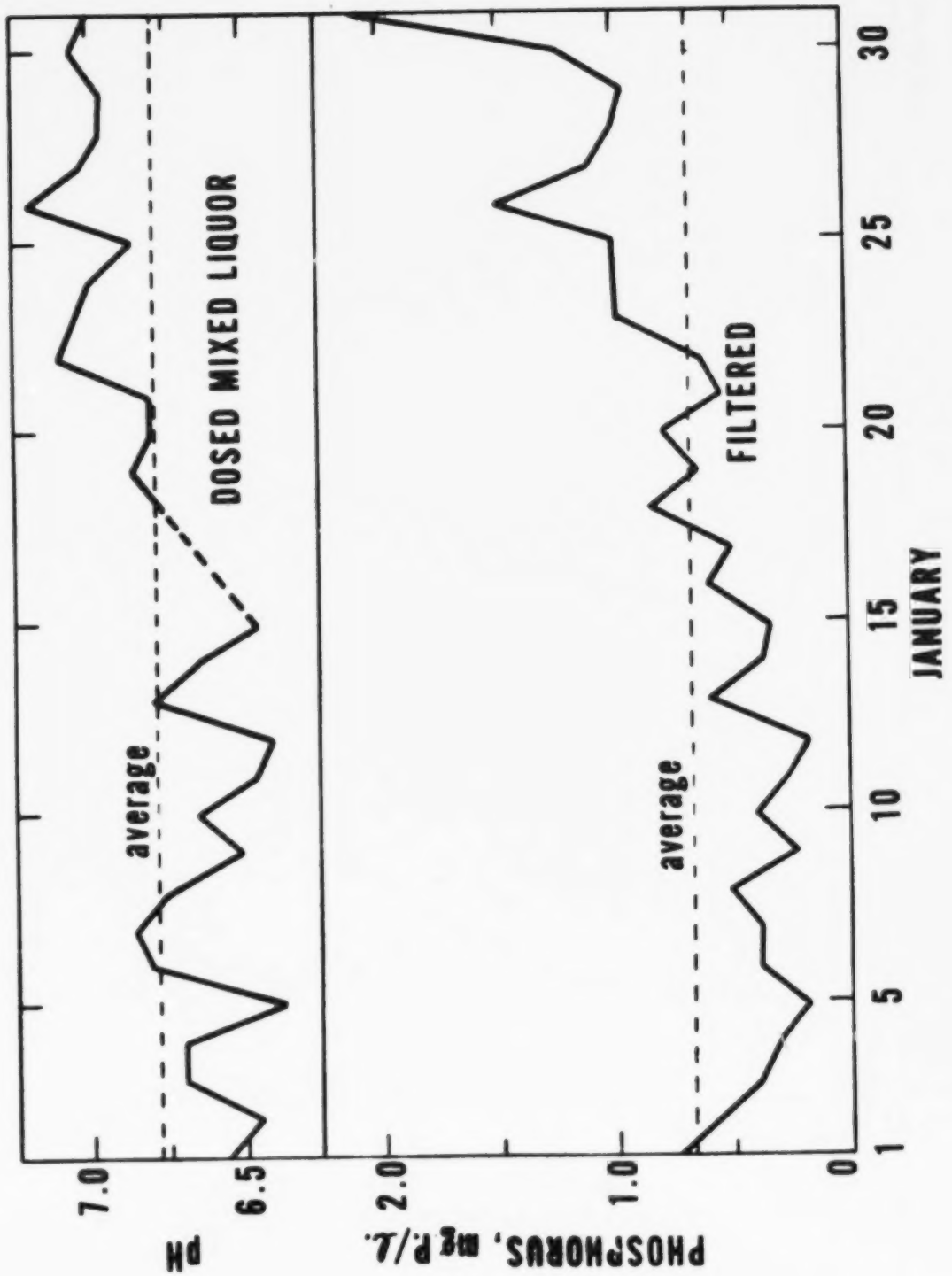

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Figure 7. Correlation between phosphorus residual fourth-stage and pH.